

THE SEARCH FOR N ON MARS: MINERALOGICAL ANALYSIS OF AMMONIUM IN CLAYS BY DTA/GC; R. L. Mancinelli, M. R. White, and A. Banin.
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Nitrogen is an essential element for life. Specifically, "fixed nitrogen" (i.e., NH_3 , NH_4^+ , NO_x , or N that is chemically bound to either inorganic or organic molecules and is releasable by hydrolysis to NH_3 or NH_4^+) is the form of nitrogen useful to living organisms. To date no direct analysis of Martian soil nitrogen content, or content of fixed nitrogen compounds has been done. Consequently, the planet's total inventory of nitrogen is unknown. What is known is that the N_2 content of the present-day Martian atmosphere is ~ 0.2 mbar. It has been hypothesized that early in Mars' history (3 to 4 billion years ago) the Martian atmosphere contained much more N_2 than it does today. The values of N_2 proposed for this early Martian atmosphere, however, are not well constrained and range from 3 to 300 mbar of N_2 [1]. If the early atmosphere of Mars did contain much more N_2 than it does today the question to be answered is, Where did it go? The two main processes that could have removed it rapidly from the atmosphere include: 1) nonthermal escape of N-atoms to space; and 2) burial within the regolith as nitrates and nitrites [2]. Nitrate will be stable in the highly oxidized surface soil of Mars, and will tend to accumulate in the soil. Such accumulations are observed in certain desert environments on Earth, such as the Atakama in Chile. Some NH_4^+ -N may also be fixed and stabilized in the soil by inclusion as a structural cation in the crystal lattices of certain phyllosilicates replacing K. Analysis of the Martian soil for traces of NO_3^- and NH_4^+ during future missions will supply important information regarding the nitrogen abundance on Mars, its past climate as well as its potential for the evolution of life. The purpose of the present study was to determine if NH_4^+ bound to clays could be detected using Differential thermal analysis (DTA) coupled with gas chromatography (GC).

DTA/GC is an analytical technique that is suitable for mineralogical analysis on landed missions to Mars. We have analyzed a variety of substances important to exobiology using DTA/GC. The substances tested in-

cluded organic compounds (proteins, amino acids), evaporites (NO_3^- , CO_3^{2-} , and NO_2^- salts), clays (montmorillonite, kaolinite, nontronite), Fe-enriched clays [3,4], non-clays (palagonite), and various mixtures of these substances. In addition, we have analyzed samples collected from ecosystems ranging from Antarctic endolithic rocks, evaporitic deposits occurring near thermal alkaline and acid springs in Yellowstone National Park, Wyoming, to gypsum halite evaporitic crusts that form along the intertidal. We compared the DTA/GC with several other techniques and found it to be appropriate as a flight instrument for the *in situ* determination of the mineralogy of the Martian surface material [5].

The DTA signature depicted in figure 1 is that of washed kaolinite with added NH_4^+ using the ion-exchange process (Banin, 1973; Gerstl and Banin, 1980). The first endotherm (~ 340 °C) in figure 1a is due to the added NH_4^+ . The endotherm occurring at ~ 500 °C is due to dehydroxylation of kaolinite, and the last sharp exotherm seen at ~ 1100 °C is the clay high temperature transition. Analyses were conducted using 30 mg of aluminum oxide as the reference material, and 30 mg of sample. Samples were analyzed using a Dupont model 1600 high temperature DTA oven equipped with a model 910 cell base. The heating rate was 10 °C min^{-1} . The system is controlled by a Sun Sparc II workstation. Further we have shown that NH_4^+ bound to palagonites and montmorillonite are also detectable

The results of this study indicate that it is possible for NH_4^+ to be bound to the ion-exchange sites of clays in a way that can be detected using DTA/GC. Future work must include methods that will enhance the sensitivity of the analyses.

References: 1. Huntten, D.M. (1993) *Science*, 259, 915-920. 2. Mancinelli, R. L. (1996) *Adv. Space Res.* 12, 241-248. 3. Banin, A, et al. (1993) *JGR* 98, 20,831. 4. Banin, A. (1973) Quantitative ion exchange process for clays. U.S. Patent Nd. 3,725,528. 5. Mancinell, R. L., et al. (1991) *Adv. Space Res.* 10, 265.

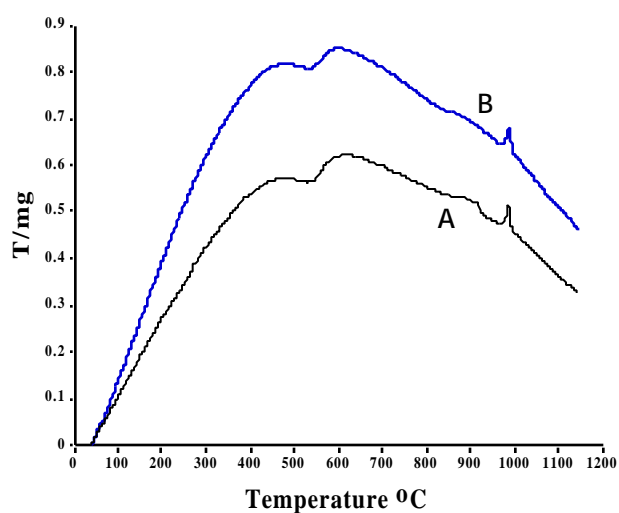


Figure 1. Results of DTA analyses of 30 mg of kaolinite containing NH_4^+ in its ion-exchange sites (a) and kaolinite containing no NH_4^+ . 30 mg of Aluminum oxide was used as the reference. The samples and reference were heated at $10^\circ\text{C min}^{-1}$. The small endotherm occurring at 340°C is due to the NH_4^+ in the ion exchange site.